Indian J. Phys **52A**, 373–378 (1978)

Structural studies and phase transitions in semicarbazide hydrochloride

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1 Introduction

Semicarbazide hydrochloride ($NH_2CONHNH_2HCl$) has been reported to be a prototype of another possible family of ferroelectrics like the addition compounds of glycine. At 293–294°K it crystallizes in the space group $P2_12_12_1$ with its constituent molecular cation ($NH_2CONHNH_3^+$) and chloride (Cl^-) anions held together in the crystal not only by electrostatic forces but also by hydrogen bonds along [001]. Dielectric measurements along [110] indicate anomalies in the dielectric constant at 43, 292 and 294°K (Rocaries & Boldrini 1972). Above 294°K the dielectric constant obeys Curie-Weiss law and this suggests that the observed phase transition at 294°K may be a ferroelectric-paraelectric transition. The X-ray studies however showed that the crystal structure does not change between 294 and 273°K. However the strong diffuse X-ray scattering from (040) plane at room temperature, which is attributed to the thermal vibrations of the molecular cation is nearly absent at 273°K. So far the existence of ferroelectricity has not been established by a direct measurement of the spontaneous polarization. The structural mechanism involved in the phase transition has been investigated through thermal and infrared studies and are discussed here.

2 Experimental

Crystal growth

Single crystals of semicarbazide hydrochloride were grown by a slow evaporation of aqueous solution saturated at 298°K. The crystals were needle shaped along [001] and the prominent forms observed were {010}, {110} and {011}.

Thermal studies

A measurement of the entropy associated with the phase transitions at 292°K and 294°K was made employing Perkin Elmer differential scanning calorimeter. Powder specimens of 5 mgm in weight were enclosed in an aluminium capsule. The heat input to the specimens were $\sim 0{\cdot}005$ milli cals/sec. Figure 1 shows the results of the measurements. It suggests that the crystal undergoes phase transitions at 280°K and 290°K. The phase transition at 280°K is more conspicuous than that at 290°K. The temperatures at which the transitions were found viz. 280°K and 290°K are different from those at which

dielectric anomalies are observed The small change in entropy suggests that the transitions are of second order

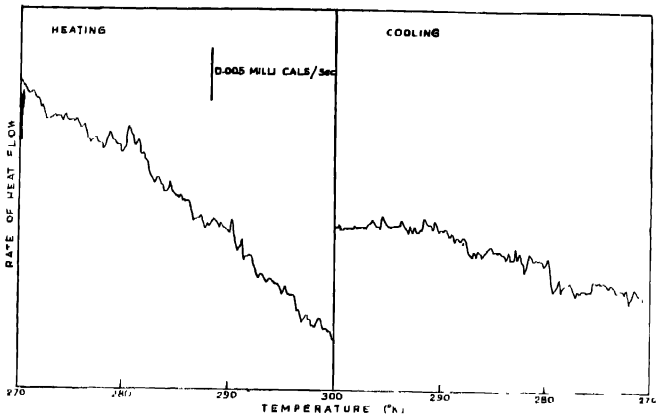


Fig. 1 Typical DSC peaks of phase transitions in semicarbazide hydrochloride.

Infrared spectra

The infrared spectra were recorded using a Carl Zeiss UR10 automatic double beam infrared spectrometer. The spectra were recorded at 300°K and below the transition at 110°K Because of the existence of the phase transition at 280°K as revealed by our thermal studies, the spectrum was also recorded at 283°K. All the spectra were recorded with the samples dispersed in Nujol mull Figure 2 shows the spectra recorded at 110°K and 300°K The spectrum at

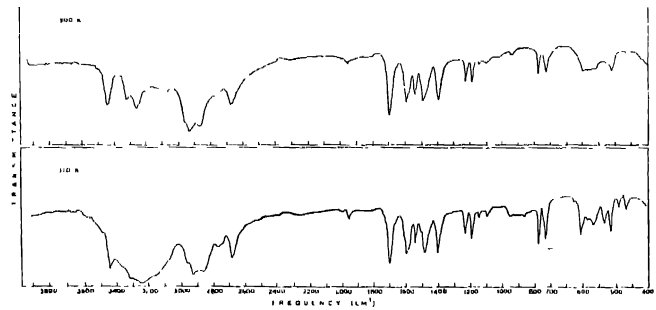


Fig 2 Infrared spectra of semicarbazide hydrochloride at 300° and 110°K.

283°K was very much similar to that at 300°K except for an increase in absorption and hence has not been reproduced

The infrared spectra have been analysed in terms of the internal modes of the molecular cation. The infrared spectrum of semicarbazide hydrochloride has been reported in the region 600–4000 cm^{-1} by Mitsuo Mashima (1964), as a part of the study of the spectra of semicarbazide and other related compounds. In the analysis of the spectra at different temperatures his assignments of the room temperature spectrum has been taken into account. The observed absorption maxima along with their assignments are given in Table 1.

Table 1. Frequencies in the infrared absorption maxima of semicarbazide hydrochloride in the region 400–4000 cm^{-1}

Assignments	110°K	300°K
	402 (m)	402 (m)
	464 (w)	464 (w)
	489 (w)	489 (w)
$\tau(NH_3^+)$	514 (m shp)	514 (m)
δ(N–N–C)	535 (m)	
δ(N–C–N)	568 (m)	575 (m br b)
	591 (w)	
	605 (m.shp)	
	625 (w)	
$wg(NH_2)$ or $t(NH_2)$	730 (m shp)	727 (m)
$\pi(O - CN_2)$	777 (m.shp)	777 (m shp)
$\delta(O = C–N)$	950 (w.b)	950 (w.b)
$r(NH_2)$	1100 (w b)	1100 (w.b)
	1140 (w.b)	1140 (w b)
$r(NH_3^+)$	1190 (m shp)	1190 (m.shp)
	1225 (m shp)	1225 (m shp)
Skeletal	1380 (sh)	1380 (sh)
	1400 (s.shp)	1385 (s)
$\delta_{sy}(NH_3^+)$	1540 (s.shp)	1540 (s)
$\delta_{as}(NH_3^+)$	1580 (sh)	1580 (sh)
	1590 (s)	1590 (s shp)
$\nu(C = O)$	1700 (s.shp)	1700 (s)
$\delta(NH_3^+) + \tau(NH_3^+)$	1960 (w.b)	1950 (w.b)
$\nu_{sy}(NH_3^+)$, $\nu_{as}(NH_3^+)$	2670 (m)	2680 (m)
	2750 (w.b)	2770 (w.b)
$\nu(NH)$	—	3070 (w.b)
$\nu_{sy}(NH_2)$	3230 (s.b)	3260 (s.b)
$\nu_{as}(NH_2)$	3320 (s.b)	3320 (s.b)
	3430 (s)	3430 (s)

ν—bond stretching δ -deformation π –out of plane deformation
b—torsional. r -rocking. wg wagging t—twisting.
sy symmetric. as— asymmetric. s strong. m—medium. w—weak.
b—band. br—broad. sh—shoulder shp—sharp.

(i) $\nu(C=O)$ · The strong band around 1700 cm^{-1} has been associated with the C – O stretching vibration. This band is found in amino acids and compounds like urea, oxamide etc.

(ii) *NH_2 Vibrations* The group NH_2 is similar to water molecule, with two stretching modes (symmetric and asymmetric) and a bending mode together with three librational modes. Usually the N-H stretching frequencies appear in the region 3100–3400 cm^{-1} while the bending is expected to appear around 1600–1650 cm^{-1}.

In semicarbazide hydrochloride a weak band around 3070 cm^{-1} and fairly strong bands around 3260, 3320 and 3430 cm^{-1} are observed. The weak band around 3070 cm^{-1} is attributed to ν(NH) and bands around that region are found in $CH_3CONHNHCONH_2$, $CH_3CONHNHCSNH_2$, $HCONHNHCSNH_2$, $(NH_2CONH-)_2$, $(NH_2CSNH-)_2$, etc The remaining bands in the region are attributed to the symmetric and asymmetric stretch of NH_2 group. Following Mitsuo Mashima, the bands at 730 cm^{-1} is assigned to $wg(NH_2)$ or $t(NH_2)$ and the weak band at 1088 cm^{-1} to $r(NH_2)$

(iii) *NH_3^+ Vibrations* : Semicarbazide hydrochloride should contain the frequencies characteristic of $-NH_3^+$ group and those frequencies could be obtained by comparison with the IR spectra of amino-acids and their salts (Shankaranarayanan 1973) Usually these compounds show two characteristic bands in the region 1500-1600 cm^{-1}, which is associated with the deformation vibrations The weak band at ~500 cm^{-1} is attributed to the NH_3^+ torsional modes and the band around 2100 cm^{-1} is known as the indicator band and is regarded as due to the combination of NH_3^+ degenerate deformation and torsional modes. Consequently the bands around 1590, 1580 and 1540 cm^{-1} which are observed in semicarbazide hydrochloride are assigned to NH_3^+ deformation and the weak band at 1950 is regarded as the indicator band The N-H stretching frequency in NH_3^+will be lower than that of the corresponding frequency in NH_2 or NH groups. Hence the band at 2670 cm^{-1} is believed to be the stretching frequency of NH_3^+ group The bands at 1190 and 1230 cm^{-1} are assigned to $r(NH_3^+)$.

The bands at 768 cm^{-1} and 950 cm^{-1} are attributed to the $\pi(O=CN_2)$ and $\delta(O=C-N)$ respectively and such bands are found in $(NH_2CONH-)_2$, $(NH_2CONHNH_2)$ etc.

The bands in the region 400–600 cm^{-1} are believed to be mainly due to NH_3^+ torsions, δ(N–N–C) and δ(N–C–N) The δ(N–C–N) in NH_2CONH_2 and (N–N–C) in CH_3NHNH_2 are found to have frequencies at 433 cm^{-1} and 556 cm^{-1} respectively.

U.V Spectrum

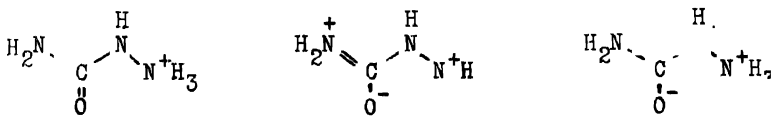
The U.V. absorption spectrum of this crystal shows a maximum at ~230 mμ characteristic of n–π^* transition in carbonyl compounds

3. Spectra Structure Correlation

The infrared spectrum at low temperature shows some interesting changes in the region 400–600 cm^{-1} where the torsional modes of NH_3^+ group are responsible for infrared absorption. The absorption bands around 514 cm^{-1} and 575 cm^{-1} are found to split and the weak bands at 464 and 489 cm^{-1} gain in intensity. The bands at low temperatures are sharp in contrast to their diffused nature at room temperature. These changes in the spectra do not appear suddenly at a particular temperature but gradually with the lowering of temperature. In contrast to the sharpening of the bands at low temperature, the bands in the region 3100–3400 cm^{-1} become broader.

The correlation between the observed changes in the spectra with that of possible changes in the structure will be discussed here.

(a) *Structure*: A knowledge of the crystal structure would be of much help in correlating the changes in the spectra with those in the structure. In semicarbazide hydrochloride, HCl is considered to attach itself to the hydrazine residue because the NH_2 group of this residue is considered to be more basic in nature than that of the group $-CONH_2$. This is in fact revealed in the crystal structure (Nardelli *et al* 1965). The organic ion ($NH_2CONHNH_3^+$) is not planar and the—NH_3^+ group is 0·44 Å away from the plane of the other heavy atoms. This is accounted for by the interaction of chloride ions with the NH_3^+ group through the hydrogen bonds N^+–H---Cl^-. Further, reasonable agreement has been found between the calculated values of the bond distances and those determined from the structure analysis by assuming the following reasonable molecular structures.



I (42%) II (43%) (15%)

The important thing to note is that in all these structures, NH_3^+ group is attached to the rest of the molecule through a single bond and can execute free torsional oscillations about that bond.

(b) *Structural changes*: Since the orientation of the NH_3^+ group is controlled by the weak forces N^+–H---Cl^-, rotational amplitudes are larger and alternate orientations of not much greater energy are possible. With the increase of temperature the rotational amplitude of the NH_3^+ group increases and they can go over to different orientations, which slightly differ in their energies.

Hence it is not surprising to find diffuse absorption in the region 500–600 cm^{-1} where absorptions due to torsional modes are expected. This is in fact supported by the observation of X-ray diffuse scattering (Rocaries & Boldrini 1972). X-ray diffuse scattering is noticeable in the region 273–298°K from many axial reflections especially for (040) which is most representative of semicarbazonium ion and thus represents vigorous molecular displacements. Below 273°K no diffuse scattering is observed indicating the freezing in of these motions.

The sharpening of the diffuse absorption bands indicate the freezing in motion of the $-NH_3^+$ group. It suggests that the NH_3^+ group is now more strongly bound to N^+–H---Cl^- bonds which prevent its free orientation. This could be brought about by the cumulative effect of libration of the molecular cation, motion of the Cl^- ion and the decreased rotational amplitude of the NH_3^+ group. The gradual changes observed in the spectra indicate that the degree of disorder is a continuous function of temperature.

Thus it appears that the hydrogen bonds have only an indirect role to play in this phase transition and this is observed in TGS and many other ferroelectric double suphates.

Acknowledgment

We would like to thank Dr. Madhusudan (Raman Research Institute, Bangalore) for his help in carrying out thermal studies. One of us (MRS) would like to thank C.S.I.R., New Delhi, for the award of a research fellowship. A. H. Rama Rao acknowledges with thanks the authorities of the National College, Basavangudi, Bangalore for granting study leave.

References

Rocaries R. C. & Boldrini P. 1972 *Applied Phys. Letts.* **20**, 149.
Mitsuo Mashima 1964 *Bull. Chem. Society, Japan* **37**, 974.
Shankaranarayanan V. N. 1973 *Ph.D. Thesis*, Indian Institute of Science.
Nardelli N., Fava G. & Giraldi G. 1965 *Acta. Cryst.* **19**, 1038.